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Temperature and frequency dependence of the electrical properties of metal alginate complexes

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Abstract : The influence of a frequency on the relative permittivity as well as the a c conductivity of metal alginate complexes (Fe^{3}, Co^{2+}, Ni^{2+} or Cu^{2+} ions) as a function of temperature has been investigated The calculated values of the activation energy obtained from the experimental data indicate that most of the metal alginate complexes behaves as a semiconducting material. The real part of relative permittivity ε'_r increases with the increase of temperature. More than one relaxation peak were obtained in dielectric spectrum with increasing temperature The γ-peak was appeared at lower temperature The appearence of β-relaxation as a small shoulder is interpreted on the basis of the different magnetic character of Cu^{2+} ion than the others α-relaxation was appeared for all complexes above 390 K. The dielectric loss ε''_r was discussed for all metal alginate complexes in view of the motion of the side chains as well as the internal rotation of the individual segmental parts of the macromolecules about the chemical bonds.

Keywords : Electrical properties, temperature and frequency dependence, alginate complexes

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1. Introduction

Polyvalent metal alginates are excellent chemically and mechanically stable complexes. Due to their stabilities, they have attracted much attention for industrial and medical applications as well as in food processing techniques [1–5]. It is well known that the alginic acid is a polyuronide comprising D-mannuronic and L-guluronic acids linked through 1–4 bonds in a linear block copolymer structure [6–8].

A previous study [9,10] of the influence of frequency on specific conductance of metal alginate gel complexes in the frequency range of 0.02–800 kHz indicates that the conductance of the gel complexes is related to the strength of chelation between metal ions and the functional groups of the macromolecular chains. Owing to the interesting character of these metal alginate complexes, we have emphasised the relative permittivity in order to shed light on the relaxation phenomena inside the samples as well as the dependence of their a.c. conductivity on the applied frequencies.

2. Experimental

The Analar grade (BDH) materials were used in this work. De-ionized doubly-distilled water was used during preparation. Metal alginates in the form of resins were prepared by the replacement of the Na^+ counter ions in the alginate macromolecules by Fe^{3+}, Co^{2+}, Ni^{2+} or Cu^{2+} ions. This process was performed by stepwise addition of the alginate salt to an electrolyte solution containing these metal ions. The solution was rapidly stirred to avoid the formation of gelatinous precipitates of metal alginate gels. After finishing the exchange process, the cation exchange resins formed were washed with water several times. The gel samples were dried over anhydrous P_2O_5 under vacuum. Some analysis [11] such as IR and X-ray diffraction were carried out to assure the formation of the complexes. The IR spectra were observed in a Pye Unicam sp3 100 spectrophotometer using ICBR pellets technique (200 ~ 4000 cm^{-1}). X-ray diffraction pattern were obtained by a Philip 1710 diffractometer Pellets of diameter 10 mm and thickness of $\simeq$ 2.5 mm were prepared using a hydraulic press at a constant pressure of 19.6 10^7 N/m^2. DTA curves of the copper alginate samples were obtained in a Shimadzu thermal analysis (model DT-40) using a heating rate of 10 K/min to get an idea about the phase transitions present in such complexes.

After polishing the two surfaces of each pellet, silver paste was deposited on the surfaces. The relative permittivity as well as the a.c. conductivity for the samples were carried out at different frequencies using R.L.C. bridge (HIOKI model 3530) over the temperature range 290–473 K. The metal alginate discs were sandwiched between two standard metallic electrodes and mounted in a specially designed electric furnace (non-inductive). The temperature of the sample was measured using K-type thermocouple connected to a Digi-Sense thermometer (U.S.A.) with an accuracy better than $\pm$ 1°C.

3. Results and discussion

The temperature dependence of the relative permittivity ε_r' for a wide range of frequencies is shown in Figure 1 (a, b, c and d) for iron, cobalt, nickel and copper alginates respectively. From the figures, it is clear that at lower temperatures there is a continuous increase in the values of relative permittivity ε_r' with increasing temperature until the maximum value is obtained (γ-relaxation) at $\simeq$ 324, 323, 326 and 338 K for Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+} alginates respectively. The maximum values of ε_r' were reduced to about 15–40% with varying

frequency from 8 up to 900 kHz for different metal alginates. As in most dielectrics at high frequency, the electric dipoles can not follow the field variation and the result is a decrease

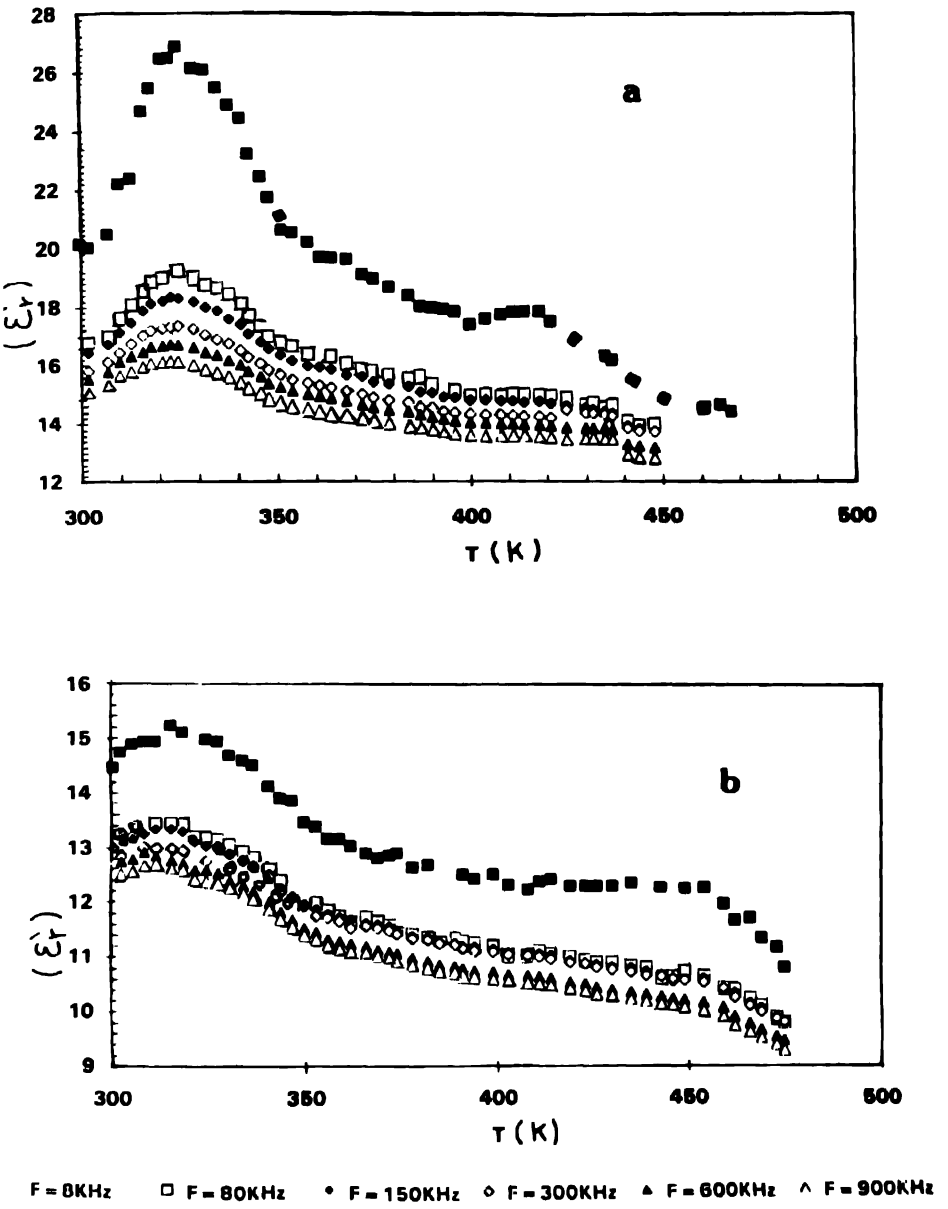


Figure 1. The relation between the real part of relative permittivity ε'_r and absolute temperature T at different frequencies for (a) Fe^{3+} and (b) Co^{2+} alginate complexes respectively.

in ε'_r. Increasing the temperature above the first peak will increase the thermal energy given to the dipoles, *i.e.* increase the degree of disorder inside the samples leading to a decrease in

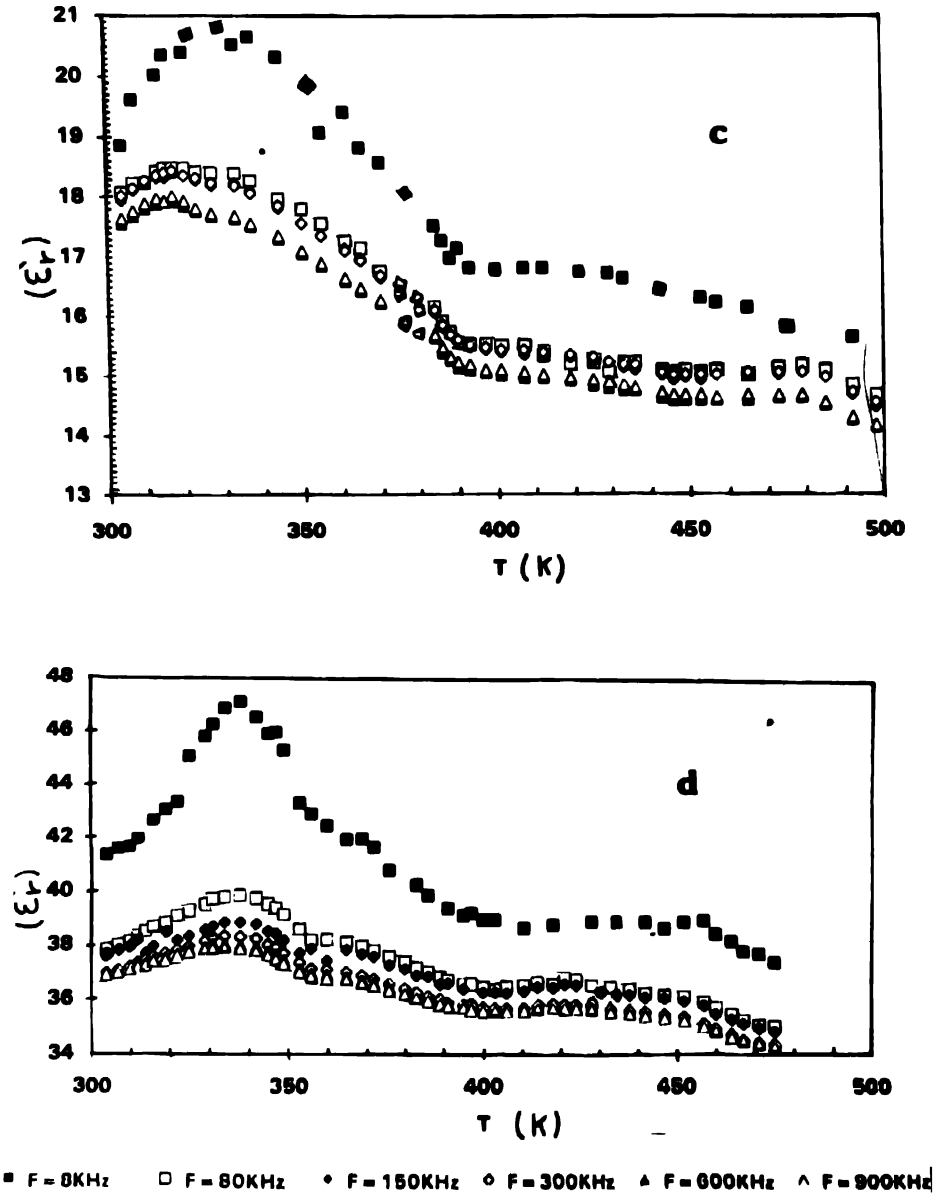


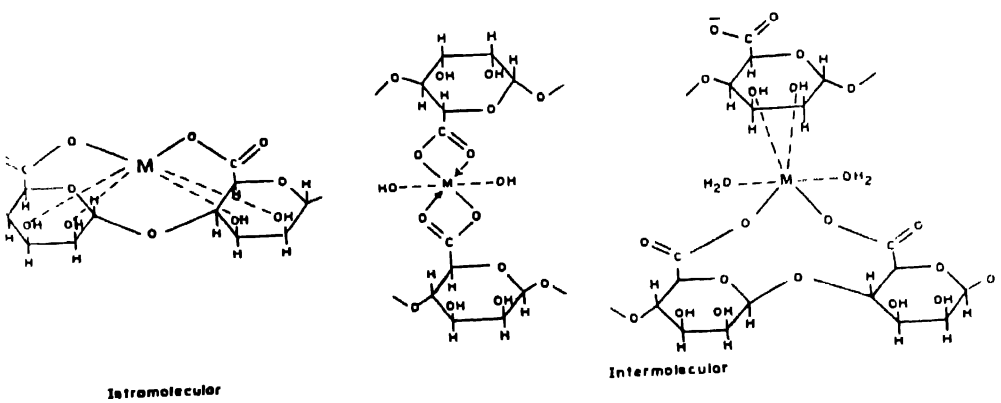
Figure 1. The relation between the real part of relative permittivity ε'_r and absolute temperature T at different frequencies for (c) Ni^{2+} and (d) Cu^{2+} alginate complexes respectively

the polarizability as well as a decrease in the relative permittivity ε_r'. The nearly constant value of ε_r' observed in that region may be due to the combined effect of high frequency and high thermal energy which produce no more dipoles [Figure 1 (a–c)].

Peculiar behaviour was observed for the Cu^{2+} alginate complex in a form of the appearance of a β-relaxation as a small shoulder at $\simeq$ 367 K which shifts towards lower temperatures, with increasing frequency in addition to the γ-relaxation peak at $\simeq$ 338 K. The existence of one unpaired electron in the 4*s*-state as well as the overlapping between the molecular orbitals of complete 3*d*-state [12] play a significant role in case of Cu^{2+} alginate compared to the other alginate complexes.

Increasing the temperature above 390 K for all samples, leads to the appearance of α-relaxation which varies in both intensity and position from one complex to another. The relaxation processes in alginate complexes (which are a type of polymers), were often studied by carring out measurements over a wide range of temperature and frequencies [9].

It is well known that divalent metal cations are in octahedral 6-coordination geometry in their complexes [13,14]. Consequently, the metal ions tend to chelate the alginate functional groups *via* inter or intra-molecular association in order to attain their octahedral geometry shown in Scheme I. However for tri-valent metal ions, the octahedral



Scheme (I)

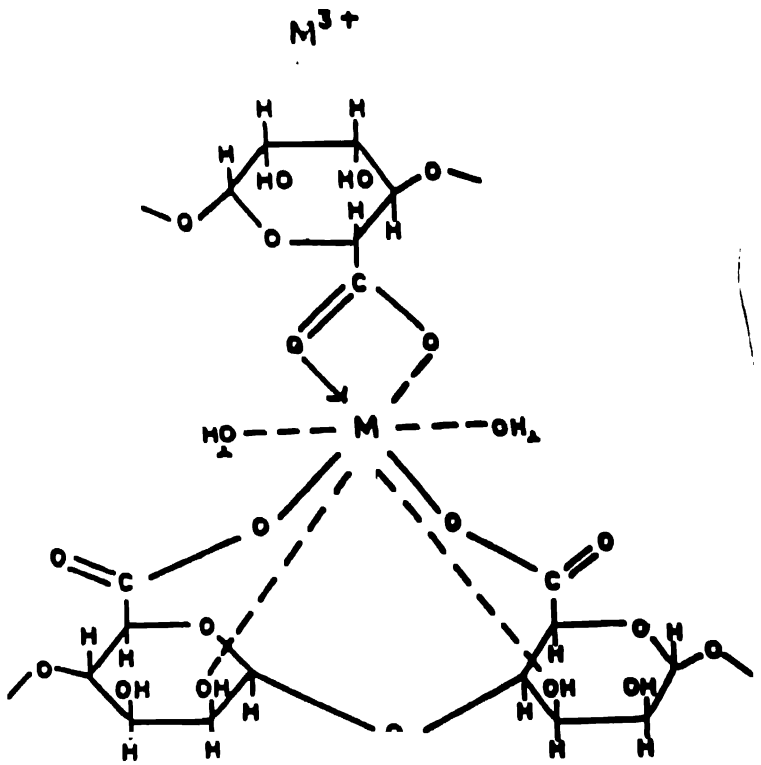
Scheme I : Chelation in divalent metal alginate complexes.

geometry can be attained *via* an intermolecular association [13,14] (Scheme II). The chelates of metal ions in case of intermolecular association, resemble an egg-box like structure [15].

The exchange process between the Na^+ counter ions of alginate macromolecules and the metal ions can be represented stoichiometrically [16,9] as follows :

$$zNa - (Alg) + M^{z+} = M - (Alg)_z + z\,Na^+,$$

where *M* is the sodium alginate polyelectrolyte and $M - (Alg)_z$ is the metal alginate complex and $z = 2, 3$.



Scheme (II)

Scheme II : Chelation in trivalent metal alginate complexes

Figures 2 (a, b, c and d) present the dielectric loss ε_r'' *versus* absolute temperature for Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+} alginate complexes respectively. A similar behaviour to that of the ε_r' *versus* T is obtained. The main feature of the ε_r'' spectra appears as a decrease in the peak height as well as a shift in position to higher temperature with increasing frequency.

In the low temperature region, the whole side groups do not have sufficient energy to vibrate, but at highe the the ufficie

vibration. The ordering of such a higher vibrating system at higher frequency, needs more energy to liberate and order them in the field. This was appeared as a shift of the peak position to higher temperature.

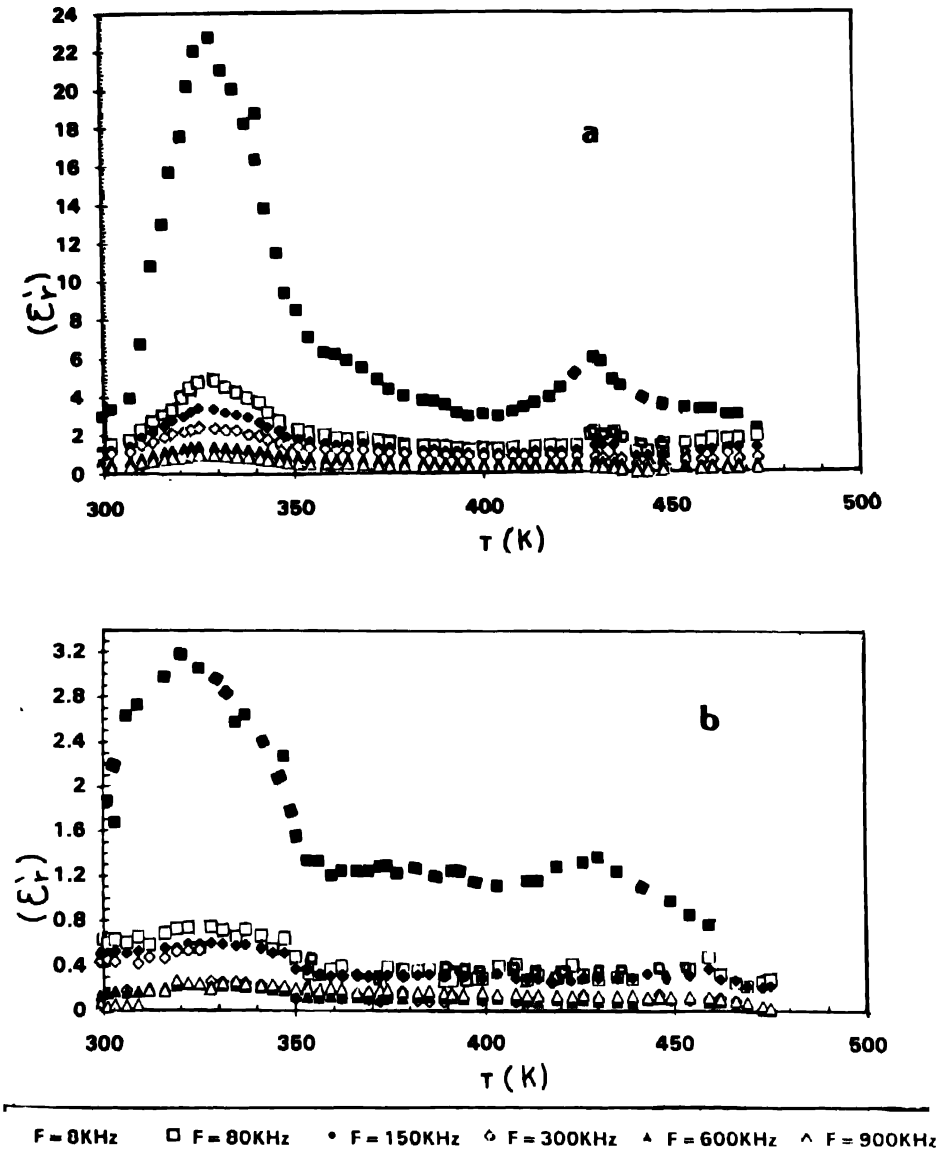


Figure 2. Temperature dependence of the dielectric loss ε''_r at different frequencies for (a) Fe^{3+} and (b) Co^{2+} alginate complexes respectively.

The appearance of the small shoulder designated by β-relaxation in case of Cu^{2+}-alginate complex is expected to overlap with the γ-relaxation for the Fe^{3+}, Co^{2+} and Ni^{2+}

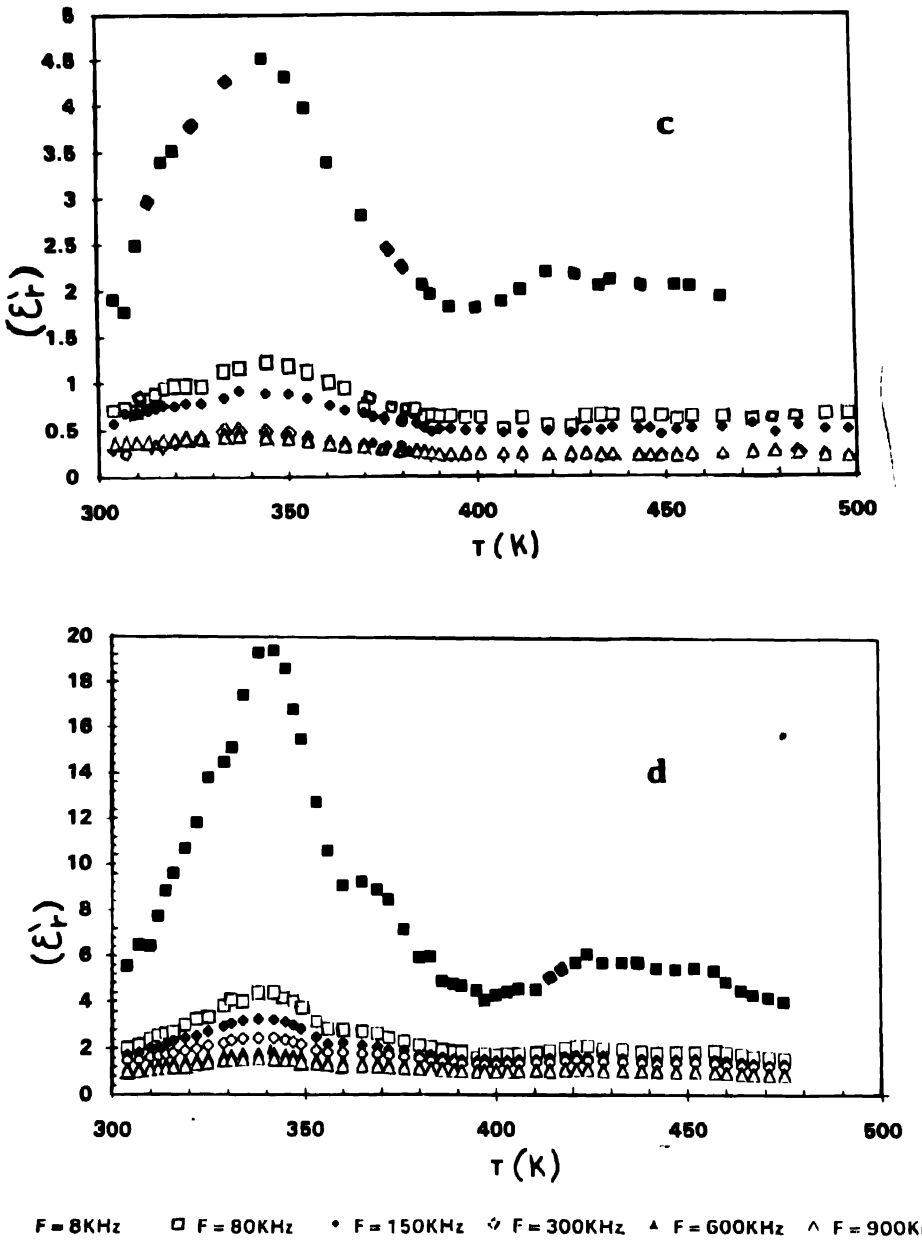


Figure 2. Temperature dependence of the dielectric loss ε''_r at different frequencies for Ni^{2+} (c) Cu^{2+} alginate complexes respectively.

alginate complexes. As mentioned above, the magnetic character of Cu^{2+} ions which differs from those of the others, enhances the appearance of the β-relaxation.

All types of relaxation obtained, is probably due to the presence of long chains which take a long time to respond to the frequency as well as the intermolecular association inside the metal alginate.

In general, two types of dielectric relaxation are possible in polymers [17] : dipolar-segmental and dipolar-group. The dipolar-segmental process is called the α-relaxation, while the β-relaxation that appeared in $\varepsilon_r'' - T$ for the Cu^{2+} alginate complex is due to the movement of the side groups and the small units of the main-chain. At lower temperature, the γ-relaxation peaks observed for the alginate complexes are expected to be due to small kinetic units of the main or side chain. In addition, the internal rotation of the individual segmental parts of the macromolecules about certain chemical bonds, will help in the above mentioned relaxation processes. Over all, the relaxation processes can be thermally activated which may involve the jump of some side groups over a potential energy barrier from one equilibrium position to another.

The temperature dependence of a.c. conductivity at different frequencies for Fe^{3+} alginate complex is shown in Figure 3. Two straight lines with two different slopes were obtained at each frequency. With increasing temperature, a main peak followed by a small shoulder is obtained. With increasing frequencies, in the low temperature region (294–333 K), the peak height was observed to increase while the activation energy is decreased. The peak position was shifted to lower temperature by varying frequency from 8 to 900 kHz. This is because the applied frequency acts as a pumping force helping in moving the charge carriers and increases the conduction. Similar behaviour was observed in the high temperature region (400–435 K).

Similar features for ($\ln \sigma - 1/T$) as that for Fe^{3+} alginate was observed in case of Cu^{2+} complex (Figure 4). A smaller activation energy is observed for the Cu^{2+} complex in both regions, than for Fe^{3+}. This means that the conduction of side groups for the Cu^{2+} complex is much greater than those of the Fe^{3+} complex due to the intermolecular association as well as the magnetic character of Cu^{2+} ions. As the charge carriers move through the alginate complex, they experience a spatial and possibly, a temporal fluctuation in local density, orientation, energy of the side groups and dipoles associated with the sample.

When comparing the values of activation energy in the low and high temperature regions (E_I and E_{II} respectively) for different alginate complexes of divalent ions (Table 1), one observes that the Cu^{2+} complex gives the higher values of activation energies at all frequencies *i.e.* lower conduction than Ni^{2+} ions of the same valence state. In general, all reported alginate complexes showed semiconducting behaviour. The intermolecular association is the most preferable one in divalent metal complexes. This in cooperation with

the small intramolecular association, establishes the character of the system. The bridging between the different ions inside the Cu^{2+} complex due to overlapping of the molecular orbitals as well as the wave function of the metal ions due to high thermal vibration will raise the conduction state and in turn, increase the conductivity.

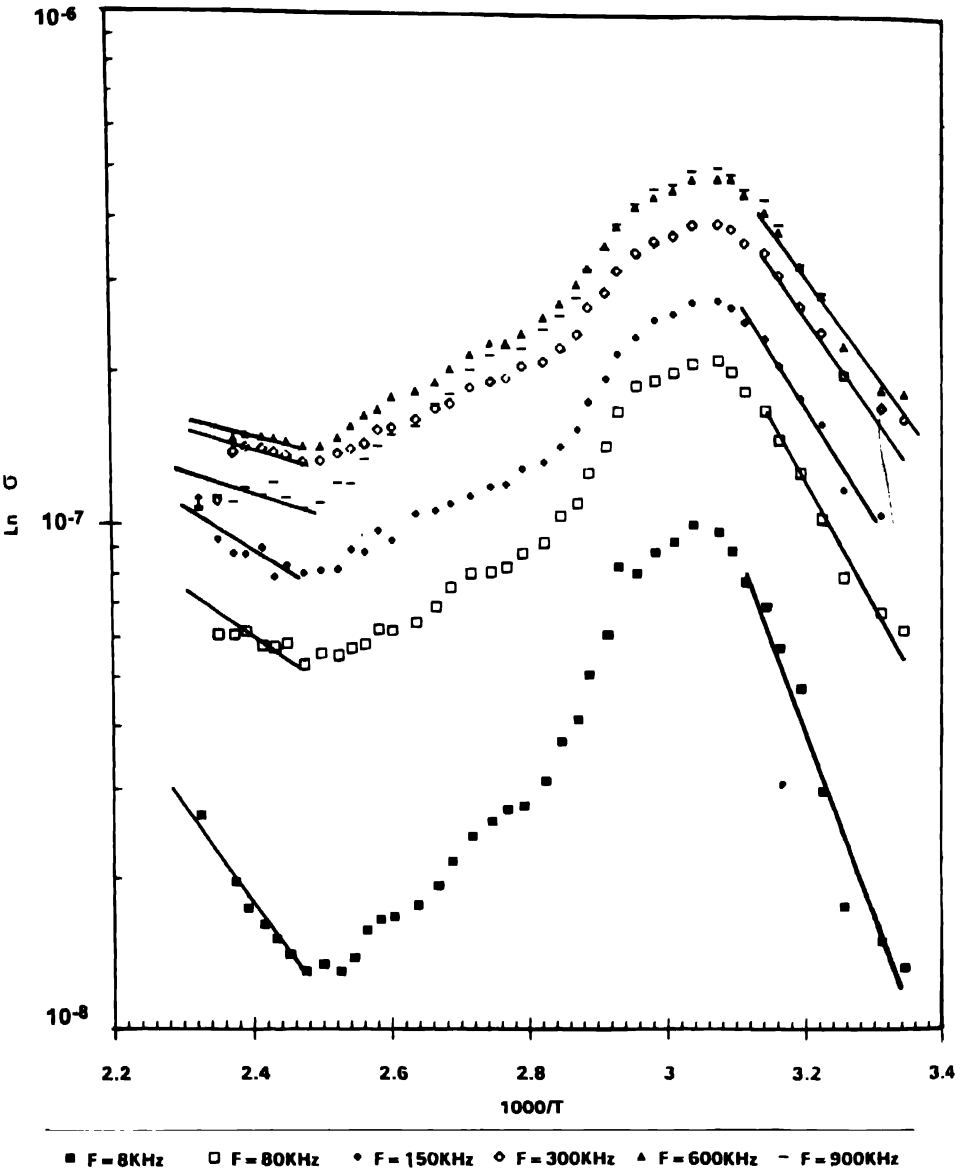


Figure 3. Plot of ln σ *versus* 1000/*T* for iron alginate complex

A closer look to Figures (3 and 4) shows that by increasing the temperature, the conductivity begins to increase due to increase of the drift mobility of the charge carriers by

heating, until it reaches a maximum at ≃ 345 K. After that the conductivity decreases with increasing temperature due to loss of water molecules from the sample. This decrease reaches its minimum value at ≃ 400 K. The conductivity begins to increase again after

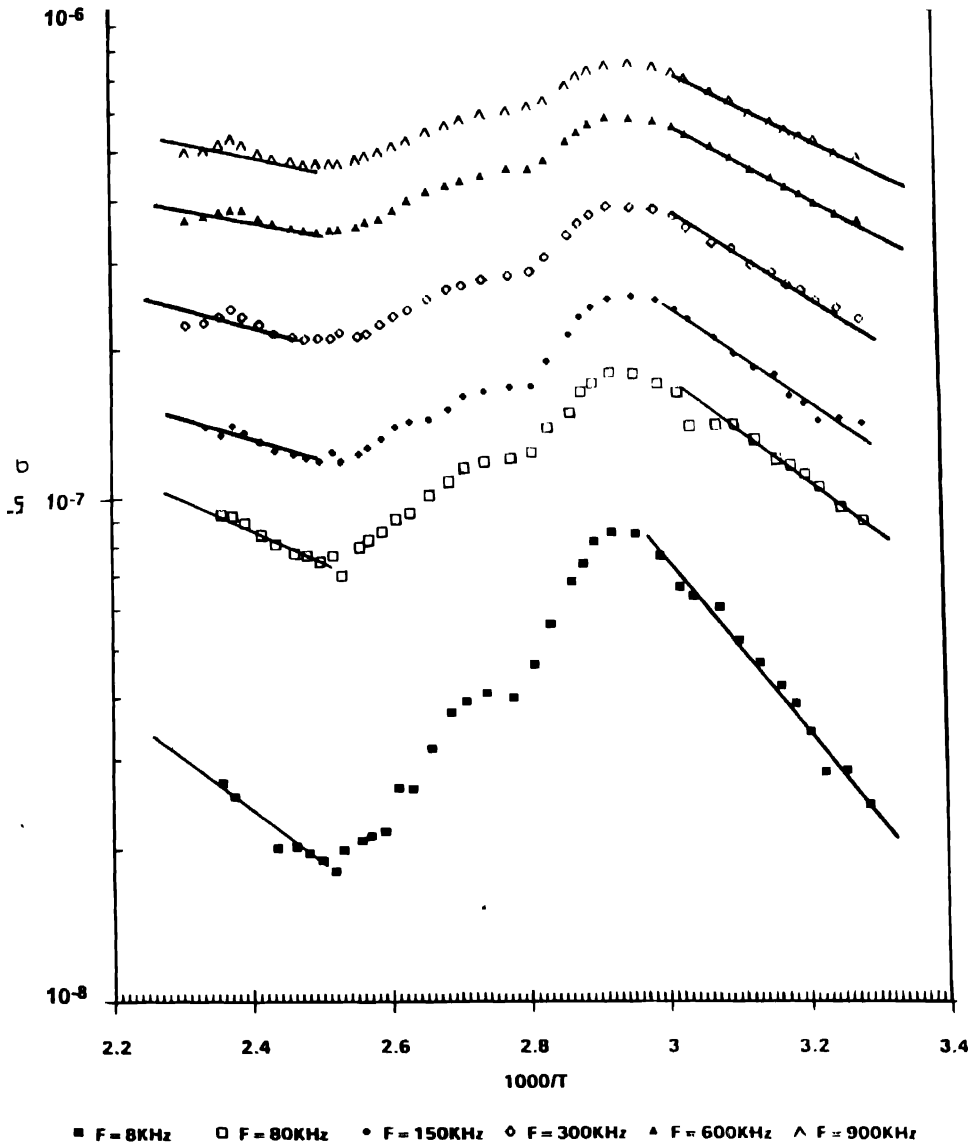


Figure 4. Plot of ln σ *versus* 1000/*T* for copper alginate complex.

400 K due to increase of thermal energy which overcomes the localization of the charge carriers and then orientation in the field accompanied with the applied frequency. At the same time, we expect some degradation to occur liberating the metal ions from their matrix. These two factors are responsible for the increase of conductivity in the

high temperature region at different frequencies. Also, the increasing in conductivity in the low temperature region may be attributed to the increase in the mobility due to unexpected change in the number of charge carriers produced from degradation at low temperature.

Table 1. Values of activation energy in the low and high temperature regions for different alginate complexes.

	Cu^{2+}		Ni^{2+}		Fe^{3+}	
F KHz	E_I eV	E_{II} eV	E_I eV	E_{II} eV	E_I eV	E_{II} eV
8	0.36	0.19	0.19	0.016	0.80	0.26
80	0.33	0.13	0.11	0.015	0.46	0.07
150	0.18	0.10	0.10	0.044	0.36	0.06
300	-	-	0.16	0.030	0.34	0.07
600	0.16	0.083	0.09	0.094	0.34	0.05
900	0.13	0.079	0.05	0.120	0.34	0.07

E_I indicates the activation energy of low temperature region.

E_{II} indicates the activation energy of high temperature region

4. Conclusion

The relative permittivity as well as the dielectric loss ε''_r have been discussed for all metal alginate complexes and are found to be dependent on the motion of the side chains as well as the internal rotation of the individual segmental parts of the macromolecules about the chemical bonds. The activation energy values indicate that most of the metal alginate complexes behave as semiconducting materials.

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